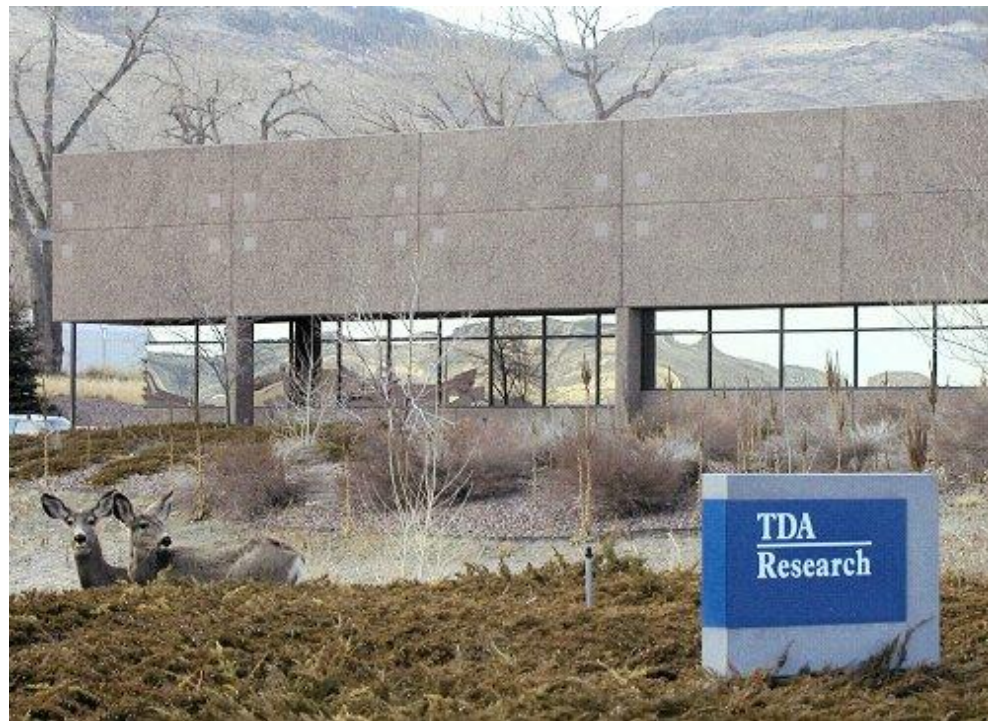


A Low Cost, High Capacity Regenerable Sorbent for Pre-Combustion CO₂ Capture

Contract No. DE-FE0000469

Project Review Meeting



**Gökhan Alptekin, PhD
Ambal Jayaraman, PhD
Robert Copeland, PhD**

**Pittsburgh, PA
August 25, 2011**

TDA Research Inc. • Wheat Ridge, CO 80033 • www.tda.com

Project Objective

- The objective of this work is to develop a new pre-combustion CO₂ capture technology and demonstrate its technical and economic viability
- A low cost, high capacity regenerable sorbent removes CO₂ above the dew point of the synthesis gas
- The sorbent is a mesoporous carbon grafted with surface functional groups that remove CO₂ via physical adsorption
- **Budget Year 1**
 - Sorbent optimization and production scale-up
 - Bench-scale evaluations
 - Process design and optimization
- **Budget Year 2**
 - Demonstrate sorbent life for 10,000 cycles
 - Slipstream demonstration using actual synthesis gas
 - Based on field data and optimum design, conduct an economic analysis to estimate the cost of CO₂ capture

Project Partners



TDA Research



Project Duration

- Start Date = November 15, 2009
- End Date = September 30, 2012
(no-cost extension is being worked out)

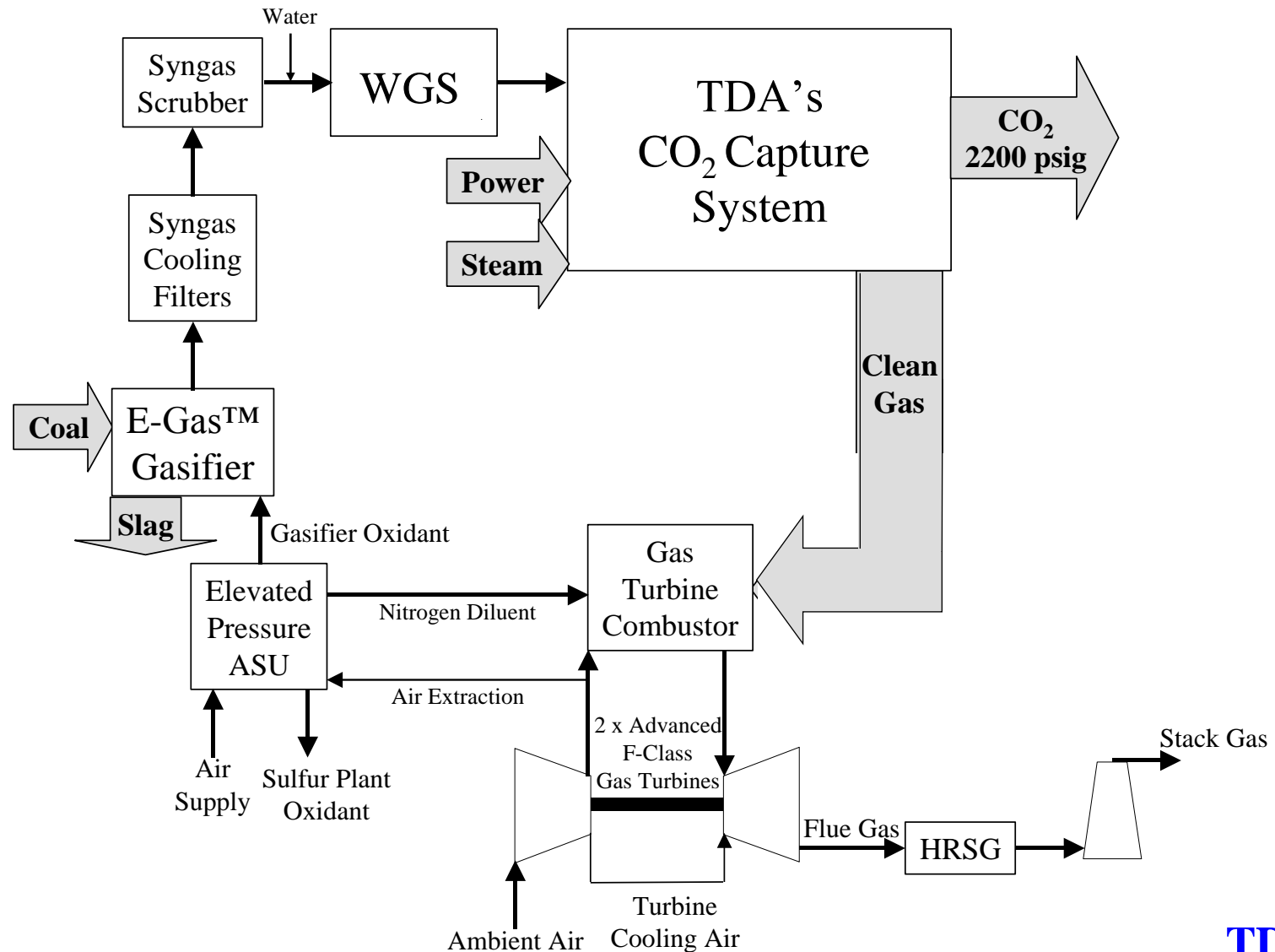
Budget

- Project Cost = \$2,500,000
- DOE Share = \$2,000,000
- TDA and its partners = \$500,000

TDA's Approach

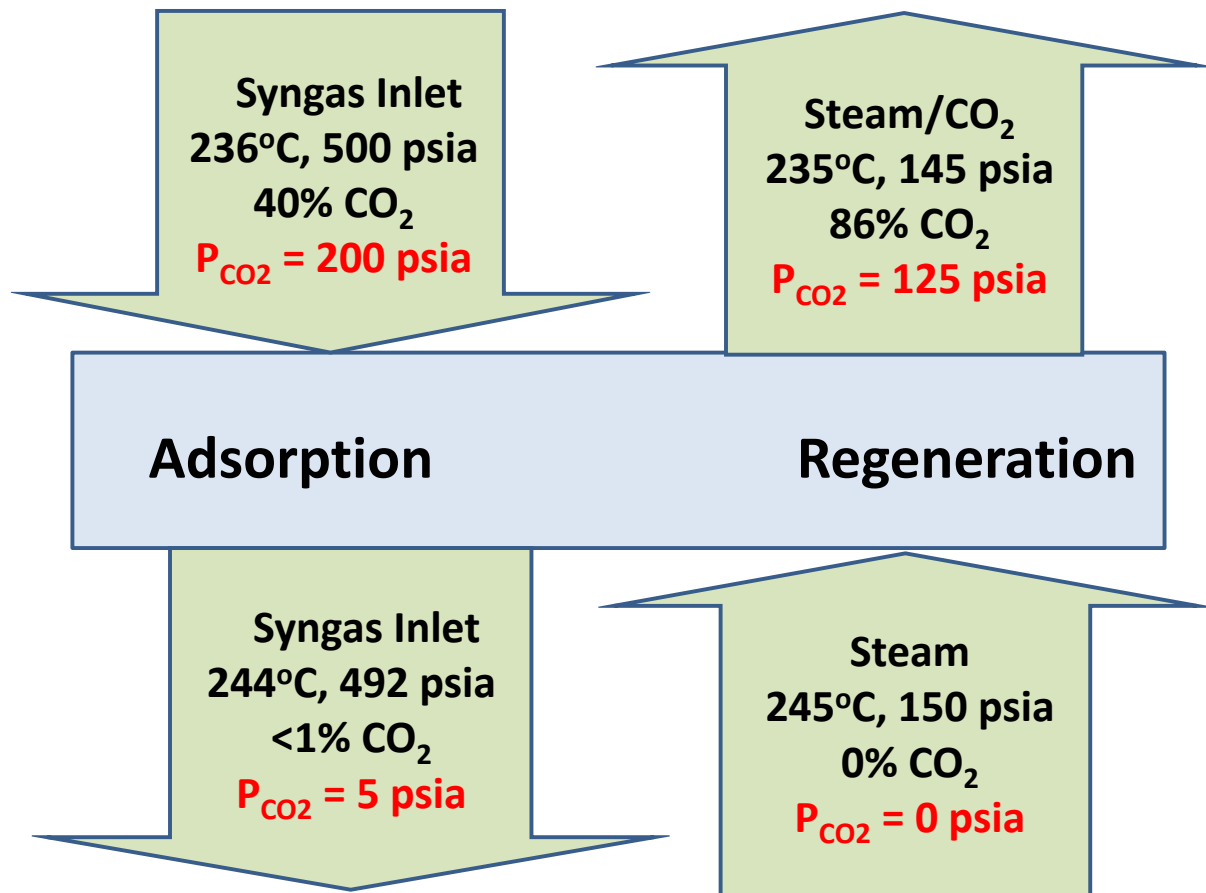
- **The sorbent consists of a carbon material modified with surface functional groups that remove CO₂ via strong physical adsorption**
 - CO₂-surface interaction is strong enough to allow operation at elevated temperatures
 - Because CO₂ is not bonded via a covalent bond, the energy input for regeneration is low
- **Heat of adsorption of CO₂ is measured as 4.9 kcal mol per mole for TDA sorbent**
 - Selexol ~4 kcal/mol
 - Amine solvents ~14.4 kcal/mol
 - Chemical absorbents 20-40 kcal/mol (Na₂CO₃→NaHCO₃ 30 kcal/mol)
- **Net energy loss in sorbent regeneration is similar to Selexol**
 - A much better IGCC efficiency due to higher temperature CO₂ capture
 - Warm gas clean-up improves cycle efficiency 2 to 4%

IGCC-Integrated CO₂ Capture System



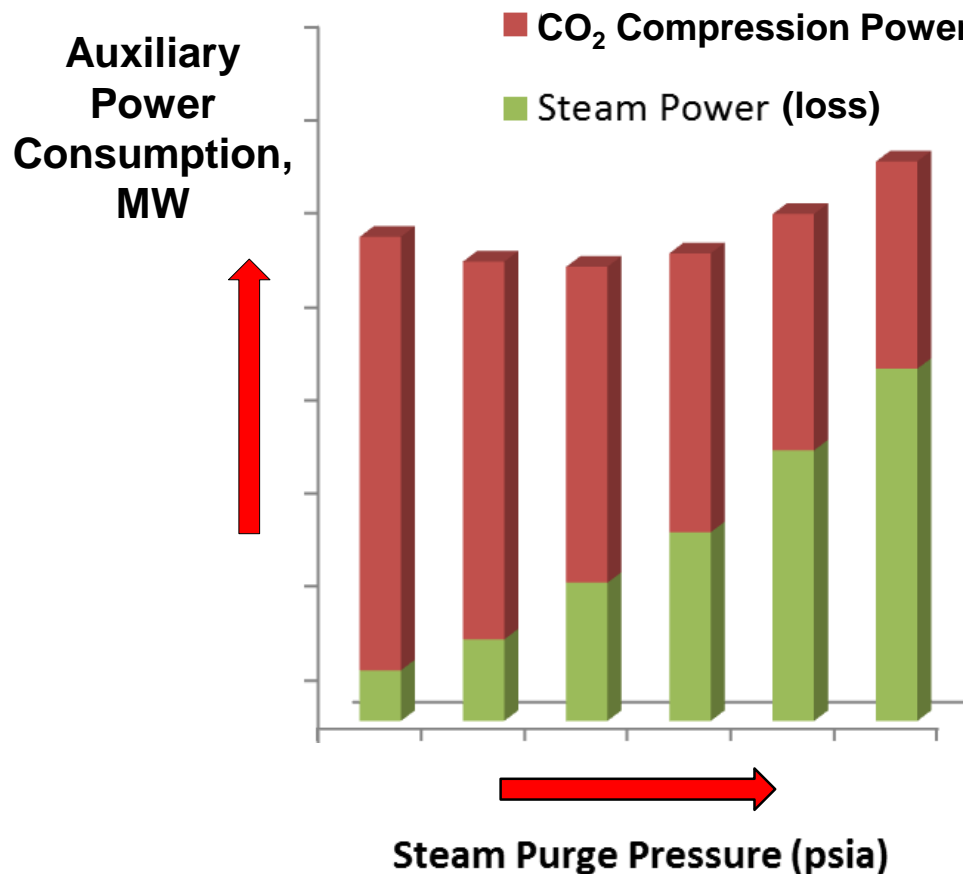
Regeneration Options

- Physical adsorbent provides flexibility in regeneration
 - Temperature swing
 - Pressure swing
 - Concentration swing
 - Combinations
- Isothermal operation is critical to eliminate heat/cool transitions which reduces cycle time and increases sorbent utilization
- Steam consumption can be reduced significantly if steam purge is carried out at low pressure



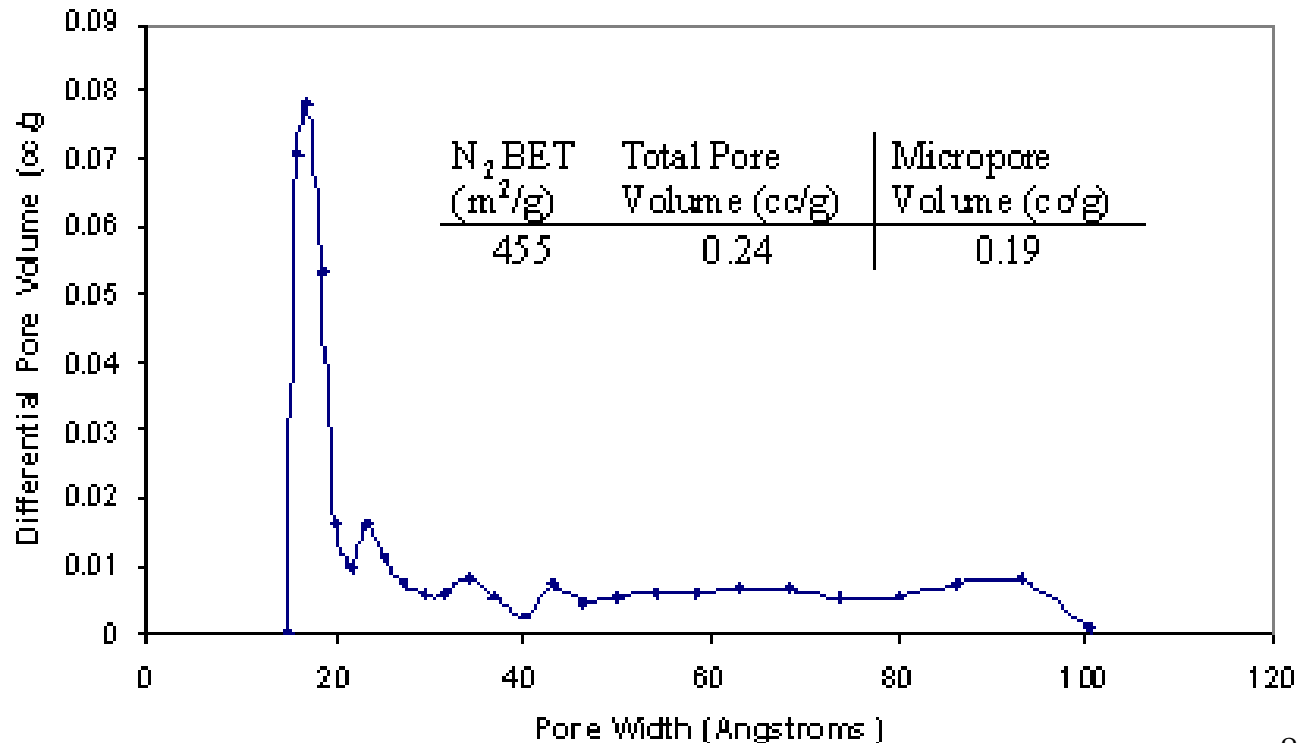
Trade-off – Regeneration Pressure vs. Steam Consumption

- Higher regeneration pressure reduces power input for CO₂ compression, while pure concentration swing requires large amounts of high pressure steam from steam cycle



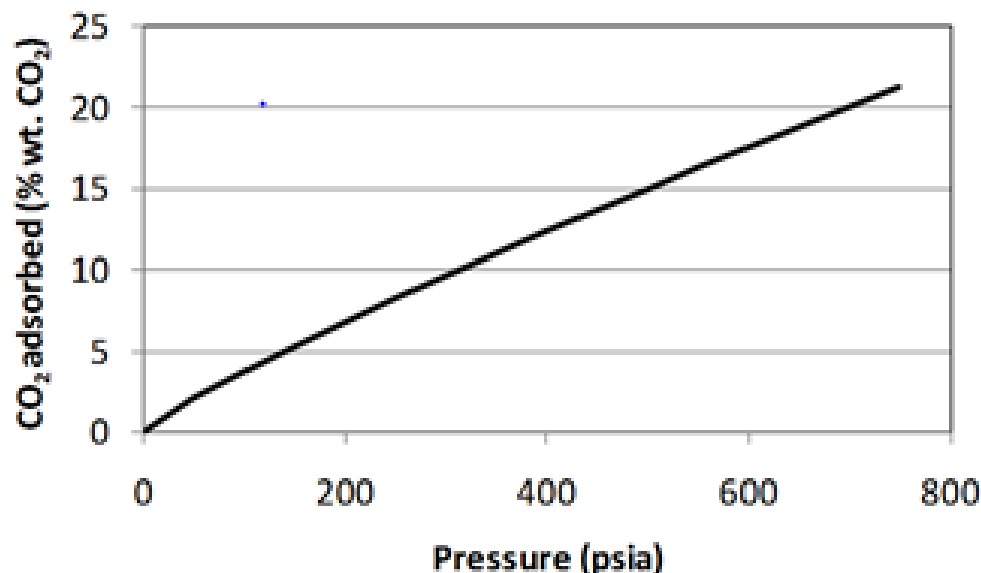
TDA's Sorbent

- **Mesoporous carbon has been developed for ultra-capacitors**
 - Meso-range pores (20 to 100 Å) are large enough to allow transport of liquid electrolyte in and out of the pores
 - Macro-porosity is avoided to achieve high surface area
 - Surface is modified with functional groups to enhance CO₂ selectivity



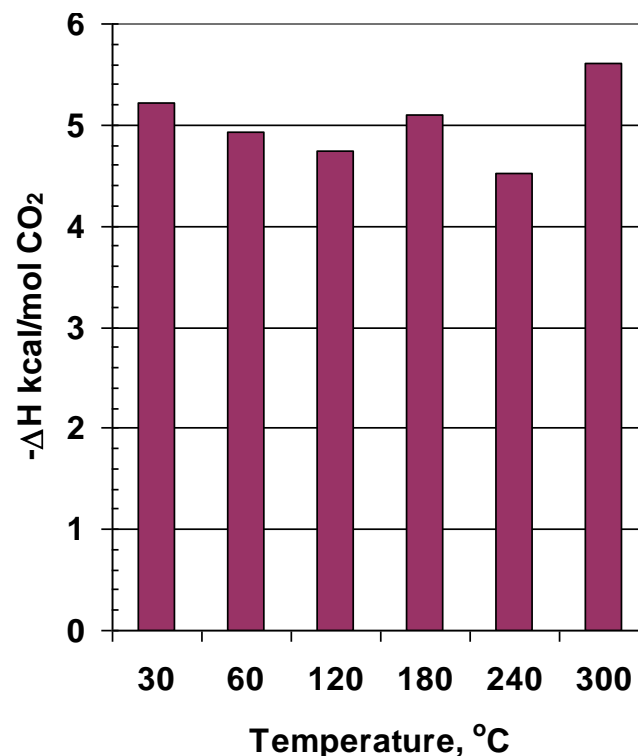
CO₂ Isotherm and Heat of Adsorption

CO₂ isotherm at 240°C



Langmuir Coefficient (q_s)	386.4 mmol/g
Langmuir Coefficient (B)	4.15E-04 1/atm
Langmuir Coefficient (n)	0.869
Diffusion Coefficient (D/R^2)	1.32E-03 1/s
Reference Temperature for B	240 °C
Heat of Adsorption (ΔH)	4.8 kcal/mol

Calorimetry Measurements



$$-\Delta H_{\text{ads}} = 4.9 \pm 0.4 \text{ kcal/mol}$$

- Isosteric heat of adsorption calculations and DSC experiments confirm the low heat of adsorption

Sorbent Production Scale-up



- Early samples are prepared using a batch process
 - 11" diameter
 - Computer controlled
 - 1000 C temp. limit
 - ~5 kg carbon/run

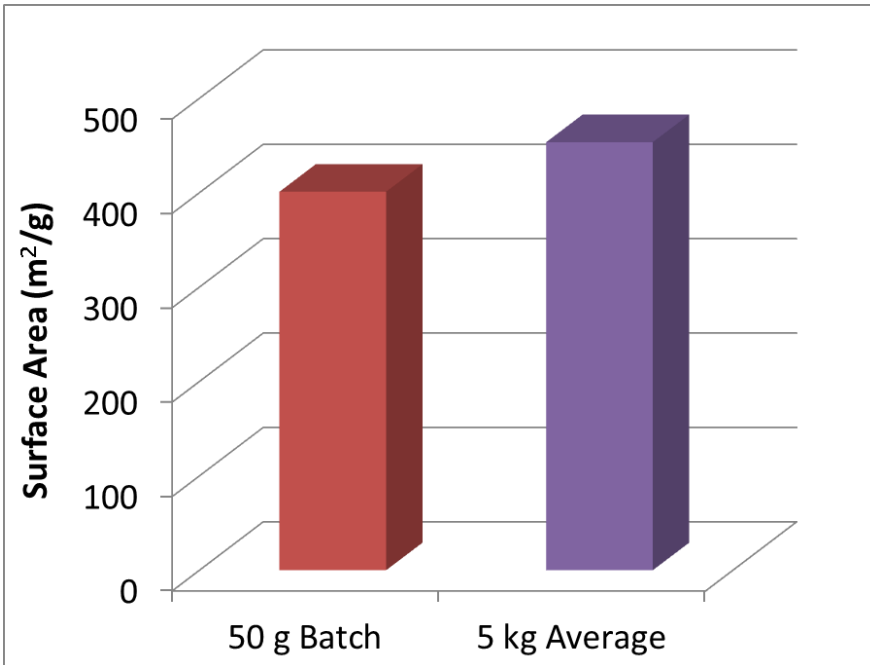


- 60 kg sorbent is prepared for field demonstrations

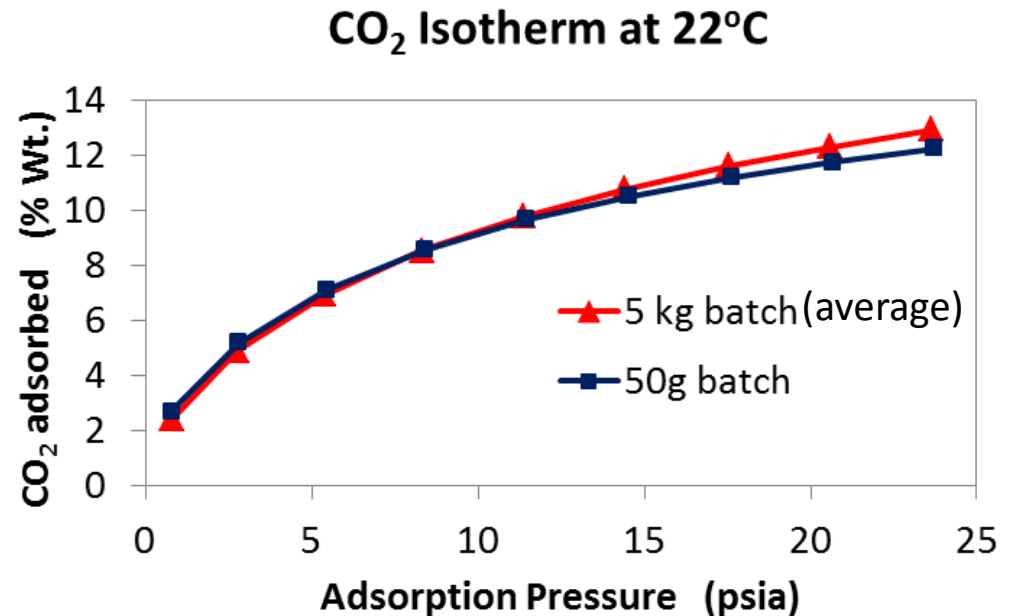


Sorbent Production Scale-up

Surface Area

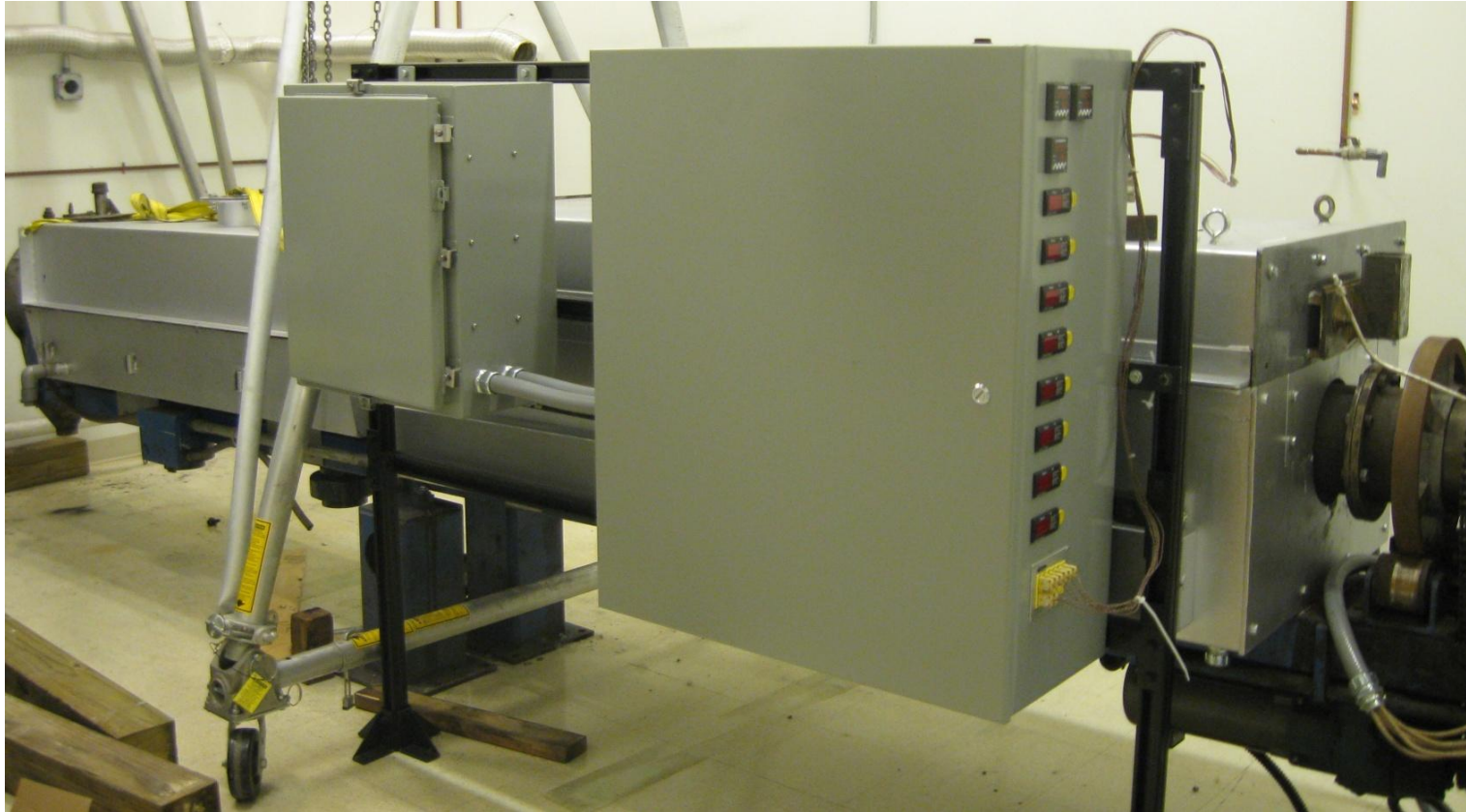


Low Temperature Isotherm



- The scaled-up sorbent showed surface area and CO₂ capacity similar to the sorbent produced at small batch size
 - Low temperature isotherms measurements were used for convenience

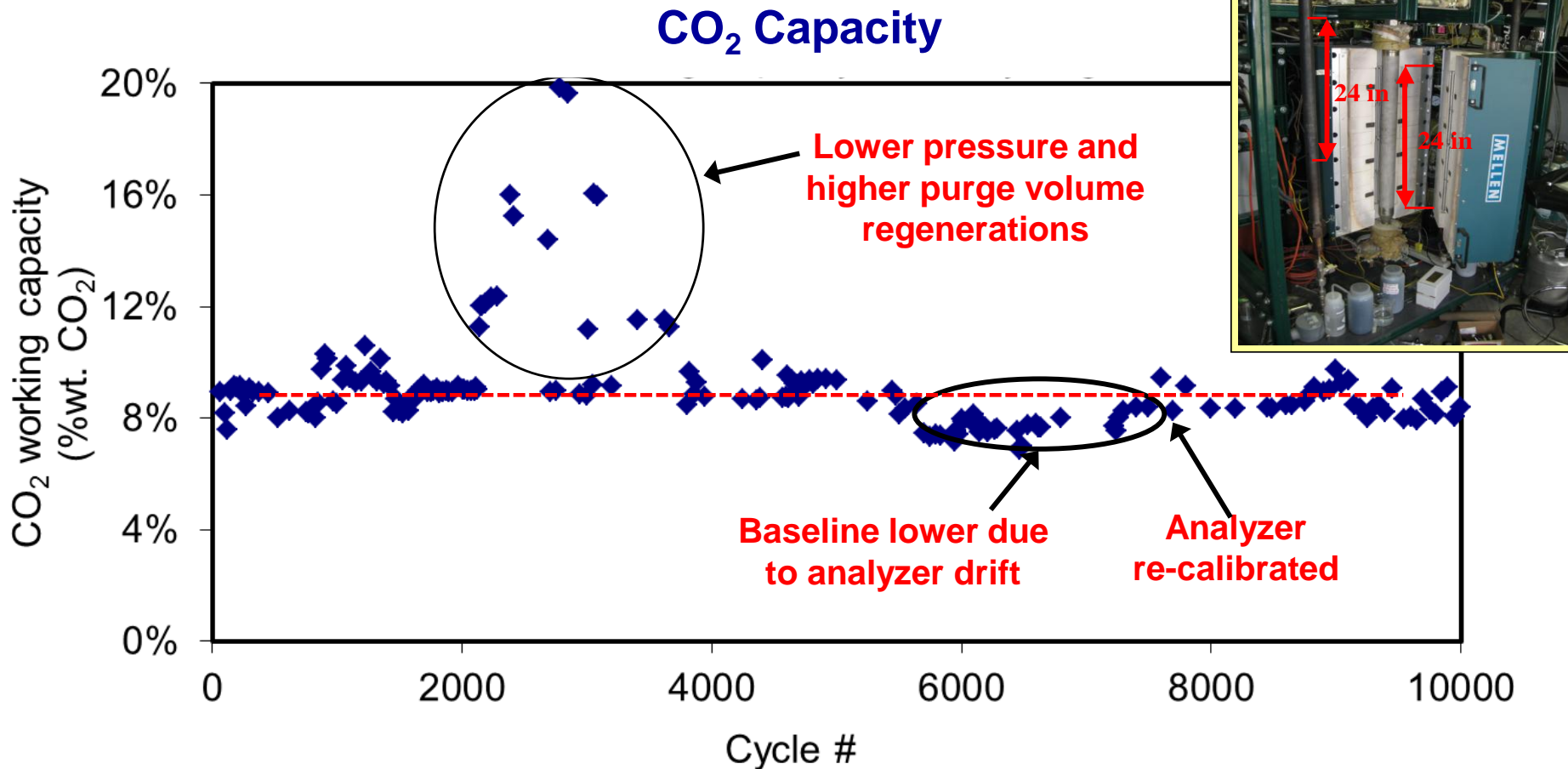
Sorbent Production Scale-up



- A continuous rotary kiln has been installed and production at pilot scale is being demonstrated
- A cost analysis is underway to estimate the cost of sorbent production

Multiple Cycle Tests

$H_2=32\%$, $CO_2=40\%$, $N_2=3\%$, $CO=1\%$, $H_2O=24\%$; $T=240^\circ C$; $P_{ads}=500$ psig; $P_{des}=50-300$ psig



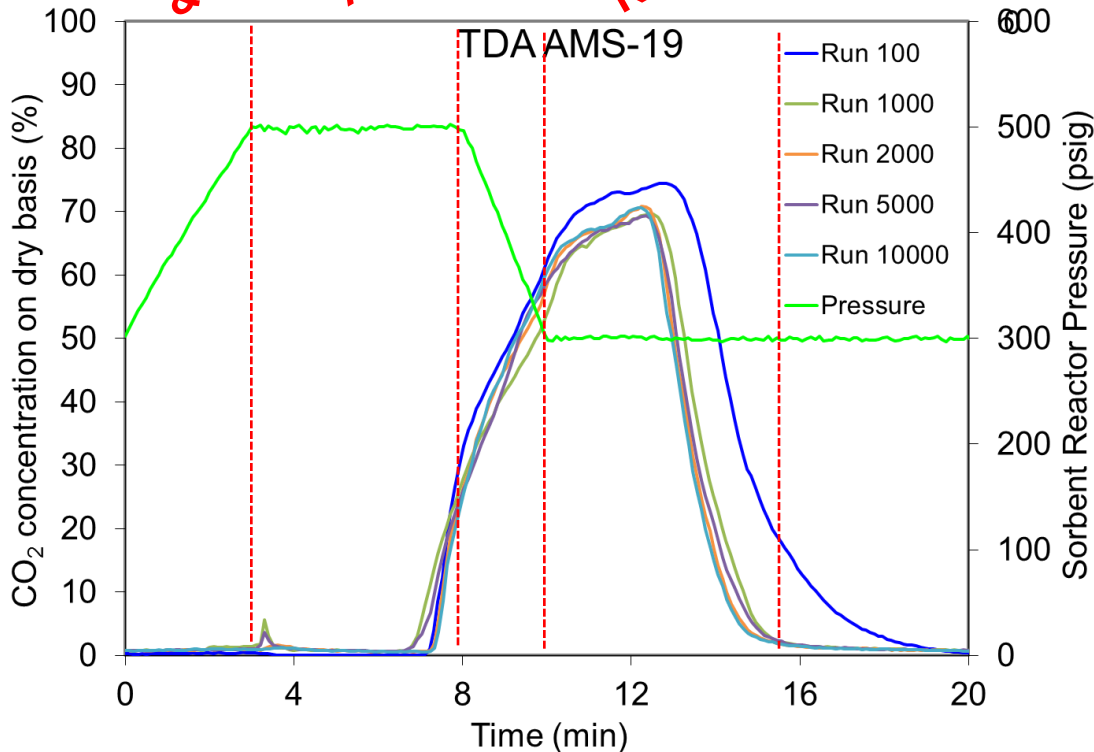
- Sorbent maintained its CO₂ capacity (8+%wt.) for more than 10,000 cycles

CO₂ Removal Efficiency

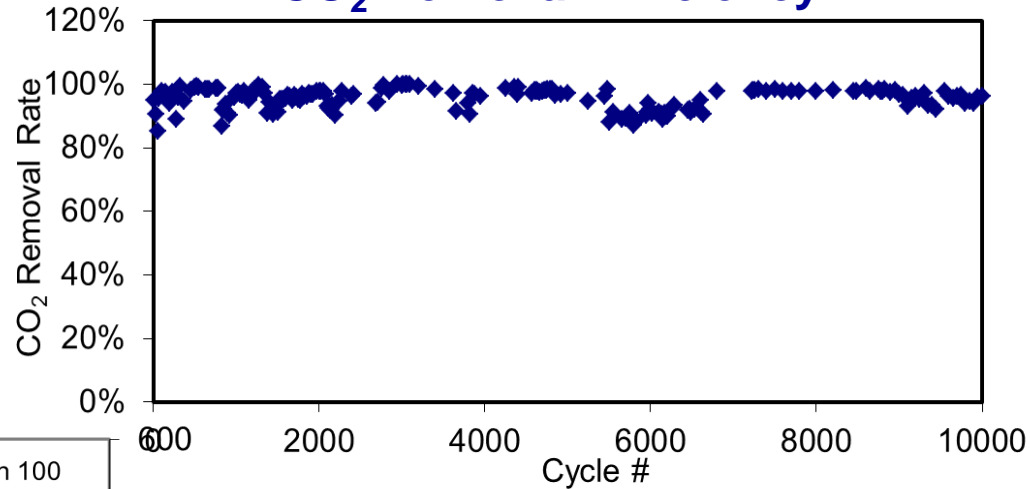
H₂=32%, CO₂=40%, N₂=3%, CO=1%,
24% H₂O; T_{ads} = 240°C ; P_{ads} = 500
psig; T_{des} = 240°C ; P_{des} = 300 psig

Pressurization
& Adsorption
Adsorption
Blowdown
Regeneration

TDA AMS-19



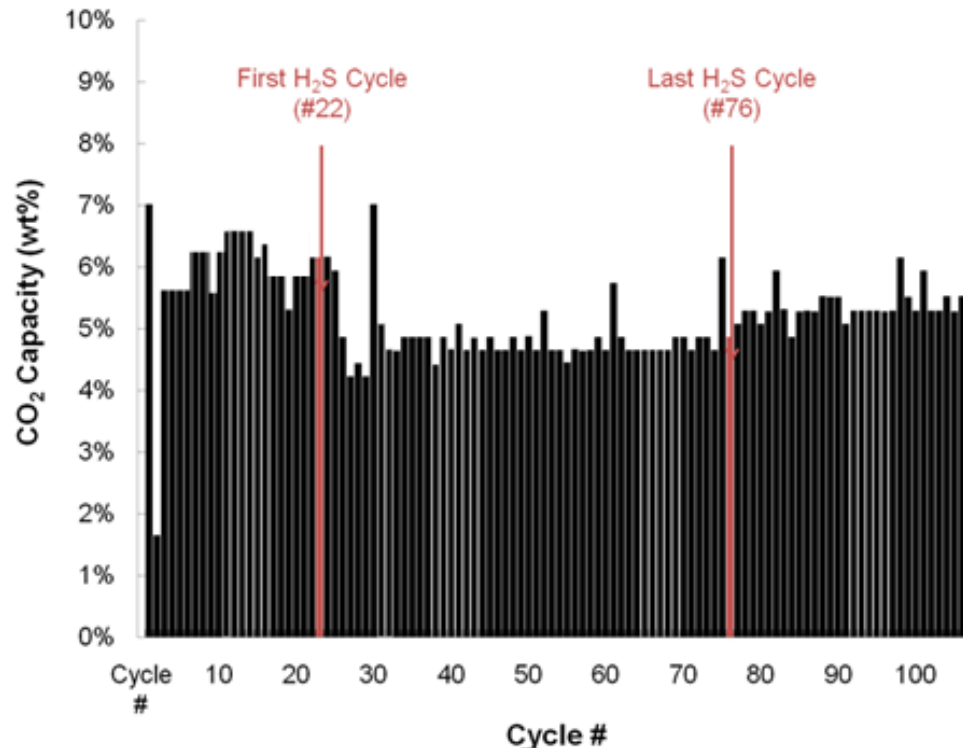
CO₂ Removal Efficiency



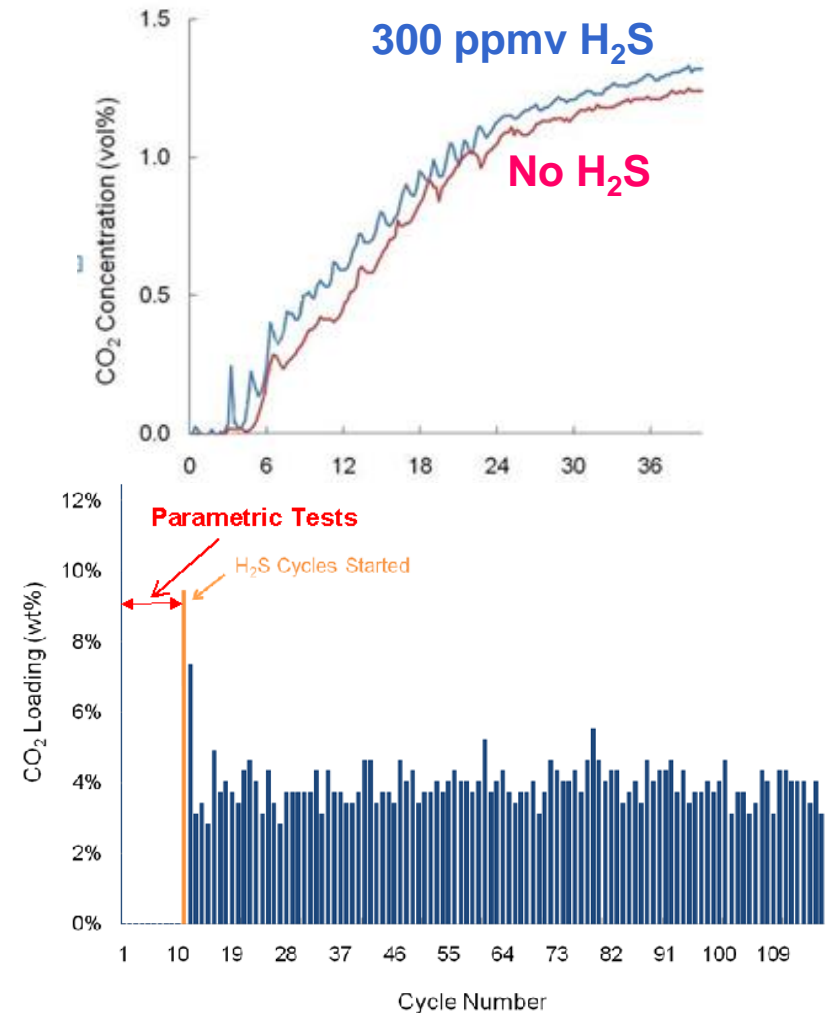
- Sorbent achieved a very high CO₂ removal rate of above 95% over 10,000 cycles

Impact of Sulfur

**T= 240°C, P= 500 psig, 10 ppmv H₂S,
44% CO₂, 20% H₂, 36% H₂O; Purge
Gas: 50% H₂, 50% H₂O**

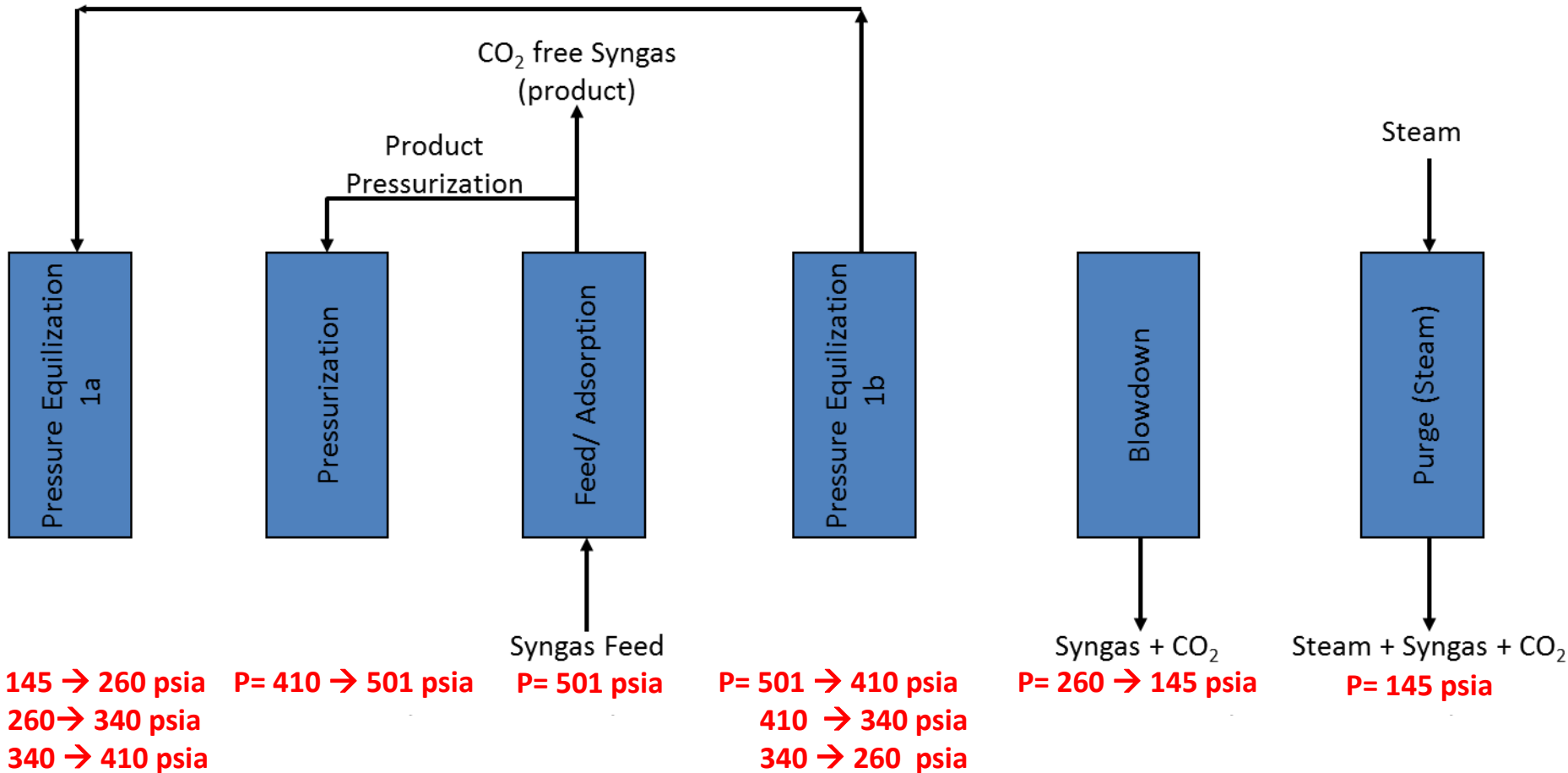


300 ppmv H₂S, T= 240°C, P= 500 psig



- **Presence of H₂S did not have a significant impact on sorbent performance**

PSA Process Design



- 3 pressure equalizations using 8 beds to minimize syngas recycle

PSA Cycle Sequence

• PSA Cycle Sequence with 8-beds

	Stage 1		Stage 2		Stage 3		Stage 4		Stage 5		Stage 6		Stage 7		Stage 8	
Time (min)	2		1	1	2		1	1	2		1	1	2		1	1
Bed 1	ADS		EQ1	HOLD	EQ2		EQ3	BD	PURGE		EQ4	HOLD	EQ5		EQ6	PRESS
Bed 2	EQ6	PRESS	ADS		EQ1	HOLD	EQ2		EQ3	BD	PURGE		EQ4	HOLD	EQ5	
Bed 3	EQ5		EQ6	PRESS	ADS		EQ1	HOLD	EQ2		EQ3	BD	PURGE		EQ4	HOLD
Bed 4	EQ4	HOLD	EQ5		EQ6	PRESS	ADS		EQ1	HOLD	EQ2		EQ3	BD	PURGE	
Bed 5	PURGE		EQ4	HOLD	EQ5		EQ6	PRESS	ADS		EQ1	HOLD	EQ2		EQ3	BD
Bed 6	EQ3	BD	PURGE		EQ4	HOLD	EQ5		EQ6	PRESS	ADS		EQ1	HOLD	EQ2	
Bed 7	EQ2		EQ3	BD	PURGE		EQ4	HOLD	EQ5		EQ6	PRESS	ADS		EQ1	HOLD
Bed 8	EQ1	HOLD	EQ2		EQ3	BD	PURGE		EQ4	HOLD	EQ5		EQ6	PRESS	ADS	

8- bed PSA Cycle Steps:

Step 1 Adsorption at 501 psia (ADS)

Step 2 Pressure Equalization to 420 psia (EQ1)

Step 3 Pressure Equalization to 340 psia (EQ2)

Step 4 Pressure Equalization to 260 psia (EQ3)

Step 5 Blowdown to 145.1 psia (BD)

Step 6 Steam Purge at 145.1 psia (PURGE)

Step 7 Pressure Equalization to 250 psia (EQ4)

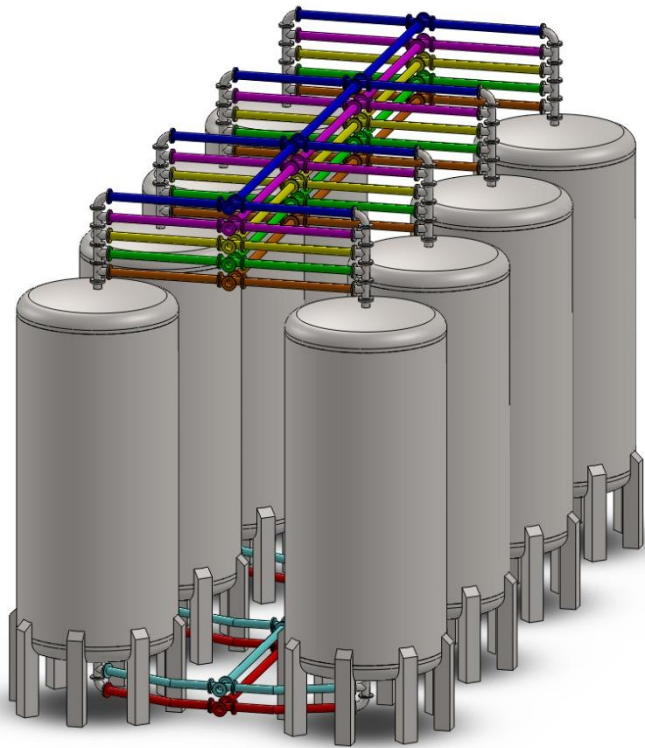
Step 8 Pressure Equalization to 330 psia (EQ5)

Step 9 Pressure Equalization to 410 psia (EQ6)

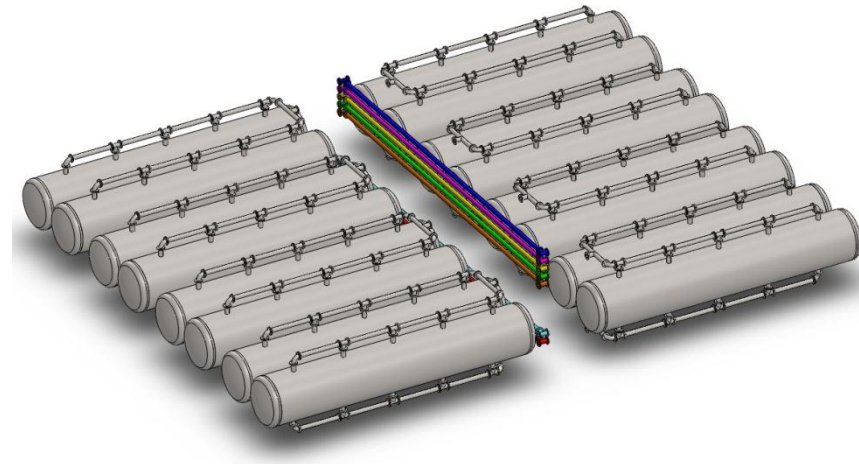
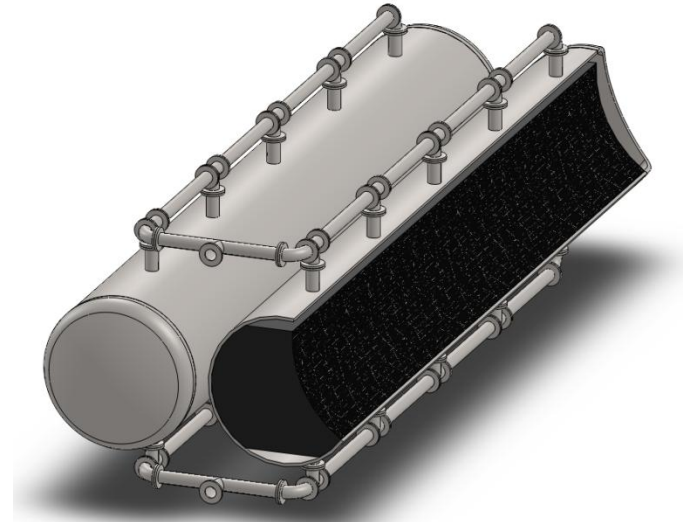
Step 10 Product Pressurization to 501 psia (PRESS)

Reactor Configurations

High L/D

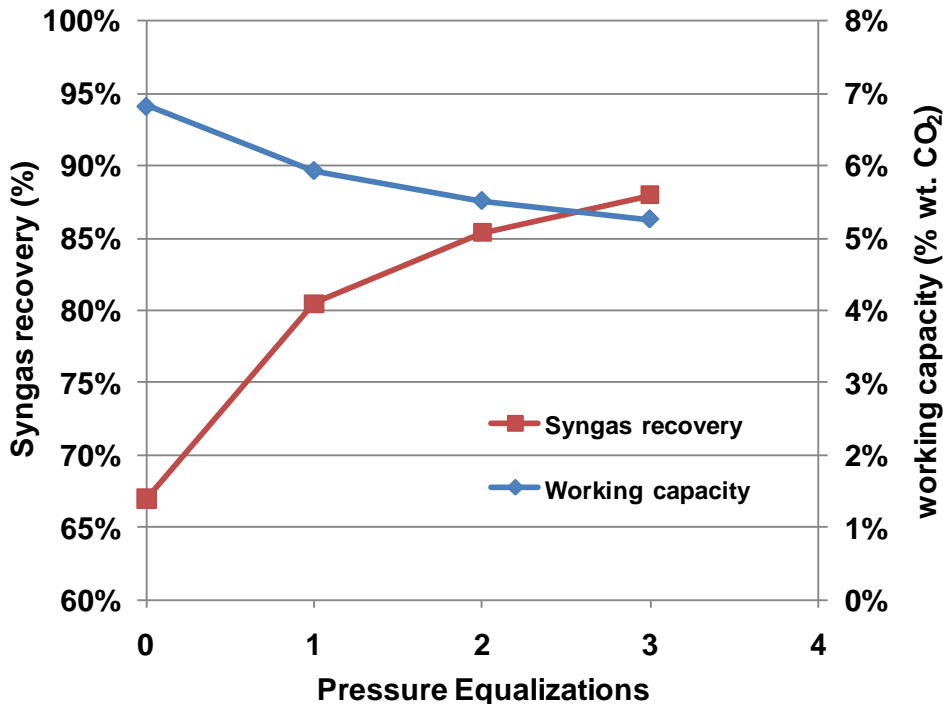


Low L/D

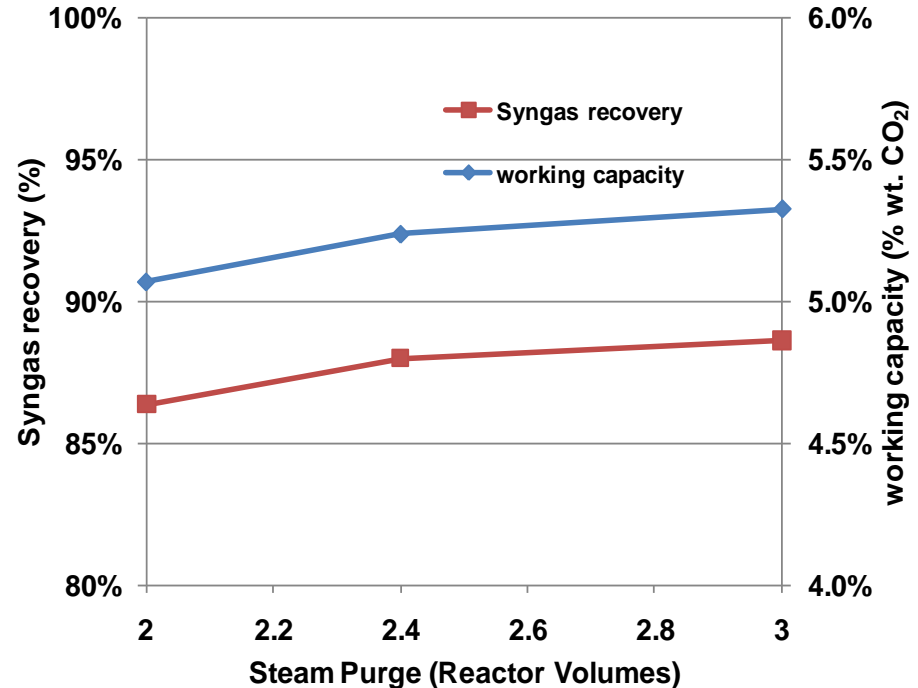


Optimization of Process Parameters

Pressure Equalizations



Steam Purge Volume

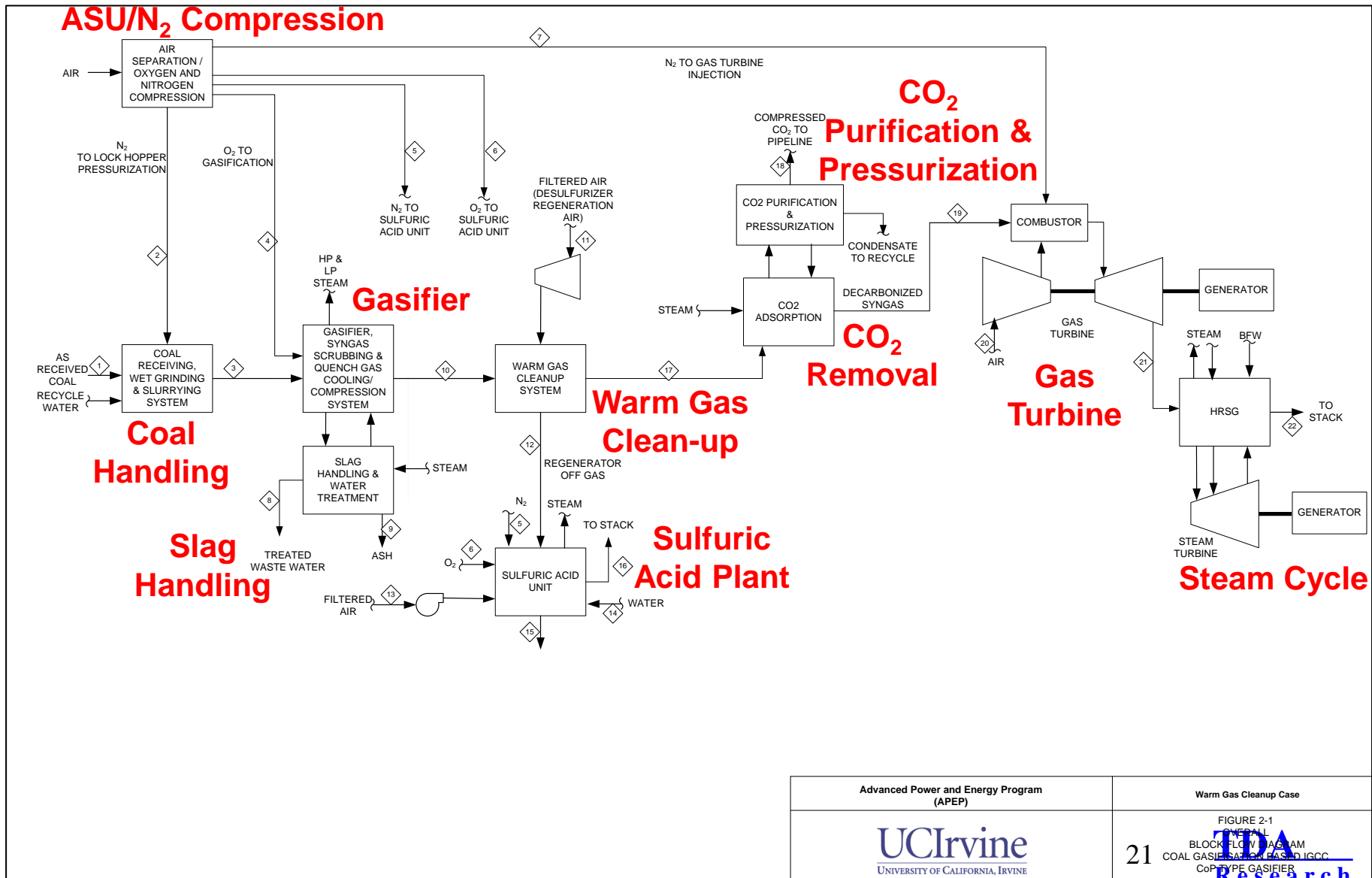


- Three pressure equalization steps are considered to increase synthesis gas recovery
 - Ensures maximum amount of syngas is used as a fuel to gas turbine
- Steam purge volume is being optimized

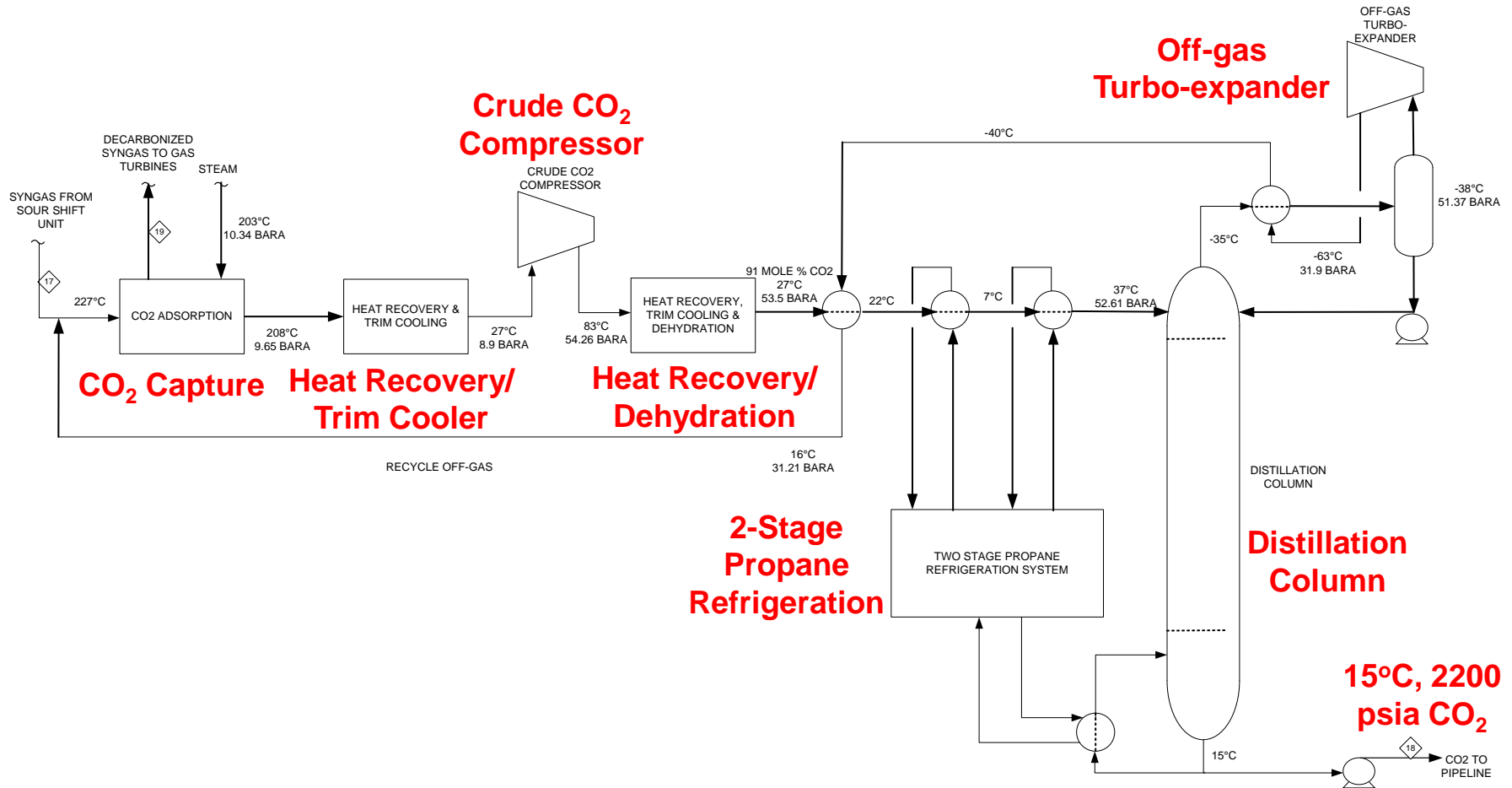
System Analysis

- UCI carries out a process simulation using AspenPlus™ and evaluate the cost CO₂ capture
- The analysis includes three simulations:
 - E-Gas™ based IGCC plant with Selexol-based CO₂ capture
 - Calibration Case
 - Compare/validate model results with prior DOE/NETL analysis
 - E-Gas™ based IGCC plant with Selexol - 90% CO₂ capture
 - E-Gas™ based IGCC plant with TDA's CO₂ capture system
- Same assumptions and cost guidelines will be adopted
 - Consistent design requirements
 - Up-to-date performance and capital cost estimates

System Modeling



CO₂ Purification & Compression



Advanced Power and Energy Program
(APEP)

UCIrvine
UNIVERSITY OF CALIFORNIA, IRVINE

Warm Gas Cleanup Case

22
FIGURE 2-2
CO₂ PURIFICATION SYSTEM
COAL GASIFICATION PLANT
COPYPE GASIFIER
Research

UCI System Analysis Results

	IGCC-Selexol Calibration Case	IGCC-Selexol 90% Capture	IGCC-TDA-WGC 90% Capture
CO₂ Capture, %	88.2	90	90
Gross Power Generated, kWe	696,770	691,624	691,460
Gas Turbine Power	464,336	461,986	459,990
Steam Turbine Power	232,434	229,638	231,470
Auxiliary Load, kWe	171,998	175,498	151,082
Net Power, kWe	524,772	516,126	540,378
Net Plant Efficiency, % HHV	32.1	31.6	33.1

- The IGCC plant with TDA's CO₂ capture technology system achieves higher efficiency than IGCC with Selexol
- Case studies exploring different design configurations on PSA operation, CO₂ purification system

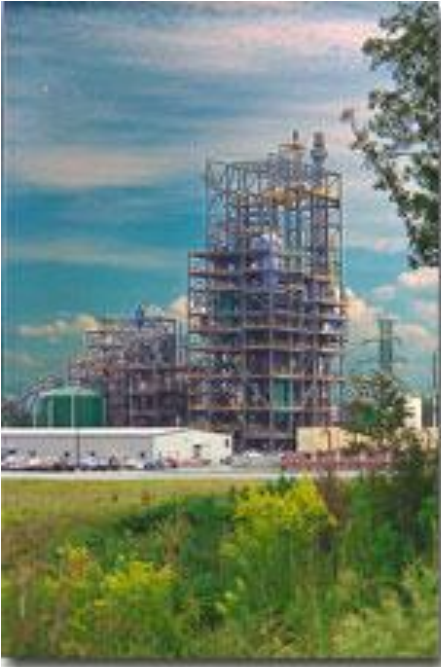
Case Studies	Plant Eff., % HHV
Case 1	32.9
Case 2	32.6
Case 3	32.5
Case 4	32.8
Case 5	32.0

Slipstream Demonstrations

- Two 3-week test campaigns for proof-of-concept demonstrations

Wabash River IGCC Plant, Terre Haute, IN

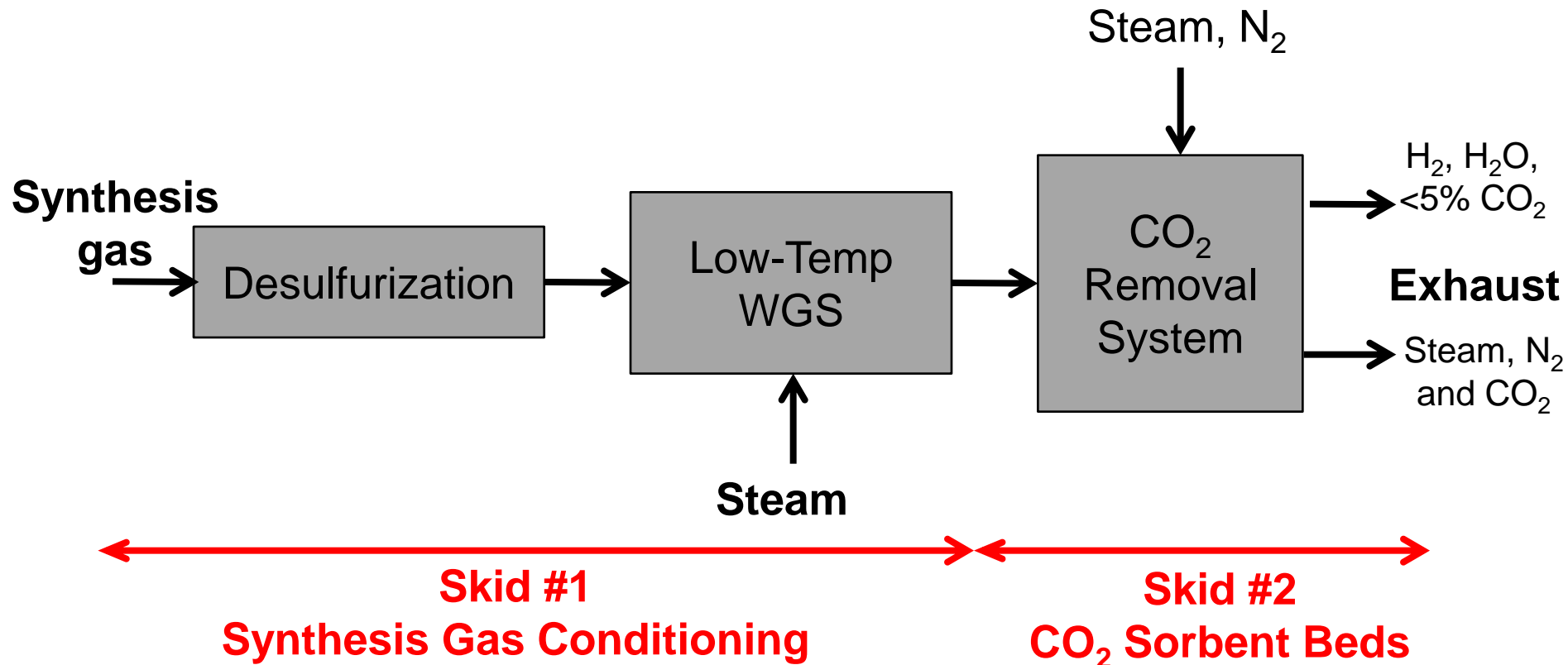
- Largest single-train gasifier with 262 MW power output
- Oxy-blown E-Gas™ Gasifier
- Operates on petcoke



National Carbon Capture Center, Wilsonville, AL

- Demonstration starts at October 10, 2011
- Pilot-scale gasifier
- Air-blown transport gasifier (based on KBR's gasification technology)
- Operates on coals and lignites

Slipstream Test Skids



- Skid #1 – Synthesis gas pre-treatment skid
- Skid #2 – CO₂ removal skid
- Skid #3 – Gas analysis skid

System Pictures – Before Insulation



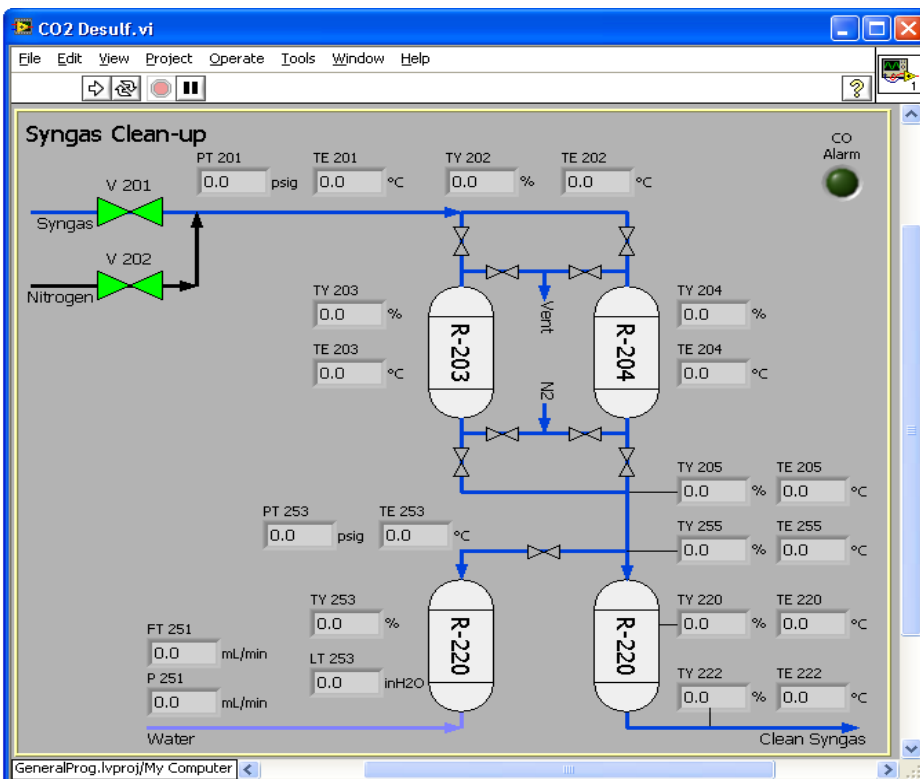
Skid #1



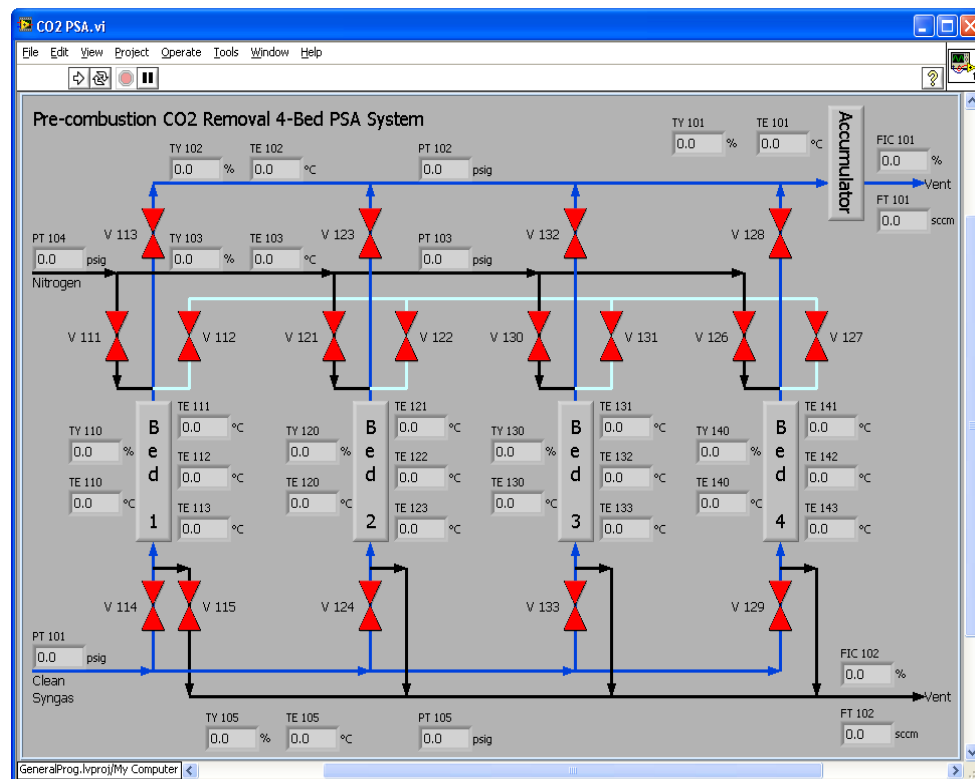
Skid #2

Control System

Skid #1



Skid #2



- System automation is complete
- Ready to move forward with slipstream demonstrations!

Acknowledgments

- **DOE Project Manager**
 - Dr. Arun Bose
- **TDA Research, Inc.**
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- **Southern Company**
 - Frank Morton
 - Tony Wu
- **MWV**
 - Paula Walmett